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(54) METHOD FOR MANUFACTURING WATER-SOLUBLE POLYMER

[There are no amendments to this patent.]

ABSTRACT

Purpose: To provide a method for smoothly manufacturing a water-soluble polymer with a high molecular weight, little insoluble portion, and excellent solubility in water by a simple operation with good productivity, using a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group.

Solution means: In the presence of an azo polymerization initiator and an inorganic phosphorus compound, an aqueous solution of a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group is polymerized by irradiating a light under the condition of a light irradiation intensity of 0.5-7 W/m², so that a water-soluble polymer is manufactured.

CLAIMS

[Claim 1] A method for manufacturing a water-soluble polymer, characterized by the fact that in a method for manufacturing a water-soluble polymer by irradiating a light to an aqueous solution of a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group, the aqueous solution of the above-mentioned monomer mixture is polymerized in the presence of an azo polymerization initiator and an inorganic phosphorus compound by irradiating a light under the condition of a light irradiation intensity of 0.5-7 W/m².

[Claim 2] The method for manufacturing a water-soluble polymer of Claim 1, characterized by the fact that the content ratio of the water-soluble monomer having a methacryloyl group in the monomer mixture is 5-35 mol%.

[Claim 3] The method for manufacturing a water-soluble polymer of Claim 1 or 2, characterized by the fact that the monomer mixture is a monomer mixture containing a ternary salt and/or a quaternary salt of acrylamide and dialkylaminoalkyl methacrylate is included at a mole ratio of the former: the latter = 90:10-65:35.

[Claim 4] The method for manufacturing a water-soluble polymer of any of Claims 1-3, characterized by the fact that the 10-hour half-life temperature of 50°C or higher is used as an azo polymerization initiator.

[Claim 5] The method for manufacturing a water-soluble polymer of any of Claims 1-4, characterized by the fact that after the light irradiation under the condition of the above-mentioned light irradiation intensity of $0.5-7 \text{ W/m}^2$, the light irradiation is further applied under the conditions of a light irradiation intensity higher than that and an integrated quantity of light of $70,000 \text{ J/m}^2$ or more.

DETAILED EXPLANATION OF THE INVENTION

[0001]

Technical field of the invention

The present invention pertains to a method for manufacturing a water-soluble polymer of the present invention. More specifically, the present invention pertains to a method for manufacturing a water-soluble polymer by irradiating a light to an aqueous solution of a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group. In the manufacturing method of the present invention, a water-soluble polymer with a high molecular weight and a small content of water-insoluble portion (hereinafter, called "insoluble portion") can be manufactured in a quick and efficient manner by a simple operation. The water-soluble polymer being obtained by the present invention can be effectively used in various applications starting with a high-molecular aggregator.

[0002]

Prior art

Since a water-soluble polymer being obtained by copolymerizing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group has an excellent aggregation performance, it can be used as a high-molecular flocculant for aggregating various kinds of waste waters, and in addition, it is useful as tackifier, sizing agent for paper-making, paper strength reinforcing agent, filtration accelerator, fiber enhancer, dyeing aid, etc.

[0003] It is known that a water-soluble polymer is manufactured by redox-polymerizing a monomer mixture containing the water-soluble monomer having an acryloyl group and the water-soluble monomer having a methacryloyl group, however since the redox polymerization requires a long polymerization time and has inferior productivity, a photopolymerization method is adopted. However, there is a difference in the reaction velocity between the water-soluble monomer having an acryloyl group and the water-soluble monomer having a methacryloyl group. For this reason, when the photopolymerization is carried out using a mixture of these two

monomers, the polymerization is not uniformly advanced, and the molecular weight of the water-soluble polymer being generated is not sufficiently high, or a large amount of insoluble portion is included in the water-soluble polymer obtained. Specifically, for example, the reaction of the water-soluble monomer having an acryloyl group such as acrylamide is not considerably advanced at the initial stage of the polymerization, and the reaction is rapidly advanced after a lapse of certain time. For example, since the reaction of the water-soluble monomer having a methacryloyl group such as salt of dialkylaminoalkyl methacrylate is slowly advanced from the initial to the latter stage of the polymerization, when the monomer mixture containing both monomers is photopolymerized, a water-soluble polymer with a high molecular weight is difficult to generate, and a large amount of insoluble portion is included in the water-soluble polymer generated.

[0004] The inventors repeatedly reviewed the above-mentioned problems caused by the photopolymerization of the monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group and pursued solutions to the problems. Then, the inventors found out a method for polymerizing said monomer mixture by irradiating a light in the presence of a specific azo polymerization initiator at the first step and irradiating a light at a light irradiation intensity of 5 times or more of the light irradiation intensity of the first step at the second step when the reflectance of the entire monomer was 95% or more and was in a specific range and [these inventors] first applied for a patent (Japanese Kokai Patent Application No. 2001-355603).

[0005] In the above-mentioned method developed by the inventors, although the monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group which have a difference in the reaction velocity is used, a water-soluble polymer with a small amount of insoluble portion and a high molecular weight can be obtained. Then, in a continuous operation by an actual apparatus using the above-mentioned method, the light irradiation intensity (especially, the light irradiation intensity at the second step) is adjusted by changing the kind of light source for an aqueous solution containing the monomer mixture. In other words, in the actual apparatus, two kinds of light sources of a light source with a small irradiation intensity for the first-step light irradiation (hereinafter, called "light source 1") and a light source with a large irradiation intensity for the second-step light irradiation (hereinafter, "light source 2") are used, several light sources 1 are arranged from the vicinity of an aqueous monomer solution charge port along a continuous belt, and a first section that meet the first-step irradiation conditions is installed. Then, several light sources 2 are arranged, and a second section that meets the second-step irradiation conditions is installed.

Then, the polymerization is carried out. The light irradiation intensity and the integrated quantity of light at the second step are changed by the adjustment of a switching position from the light sources 1 to the light sources 2 (that is, the adjustment of the length of the first section (the number of light sources installed in the first section) and the length of the second section (the number of light sources 2 installed in the second section)). However, in the continuous polymerization by the actual apparatus using the above-mentioned method, if it is necessary to switch patterns (for example, the change of the ratio (copolymerization ratio) of the water-soluble monomer having an acryloyl group and the water-soluble monomer having a methacryloyl group, etc.), it is necessary to switch the kind of light source from the light sources 1 to the light sources 2 or to switch the kind of light source from the light sources 2 to the light sources 1 to adjust the switching position from the light sources 1 to the light sources 2 each time the patterns are switched. For this reason, the polymerization operation is complicated, and there is a room for improvement in terms of practicality.

[0006] Also, methods for manufacturing a water-soluble (meth)acryl group polymer by photopolymerizing a cationic (meth)acryl group monomer or a monomer mixture containing it are proposed (Japanese Kokoku Patent Nos. Sho 54[1979]-39435, Sho 55[1980]-11684, Hei 5[1993]-53804, and Hei 7[1995]-10896). However, in these methods, a water-soluble polymer with a high molecular weight could be obtained if the content ratio of the water-soluble monomer having a methacryloyl group in the monomer mixture was less than 35 mol%.

[0007]

Problems to be solved by the invention

The purpose of the present invention is to provide a method for smoothly manufacturing a water-soluble polymer with a high molecular weight, little insoluble portion, and excellent solubility in water by a simple operation with good productivity, using a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group. Furthermore, the purpose of the present invention is to provide a polymerization method with excellent operability and high productivity that is not required to change the light irradiation intensity (the kind of light source) each time patterns are switched (especially, the change of the copolymerization ratio of monomers), when a water-soluble polymer is manufactured by a continuous polymerization of a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group, using an actual apparatus.

[0008]

Means to solve the problems

As a result of repeated review by the inventors to achieve the above-mentioned purposes, it was discovered that in manufacturing a water-soluble polymer by irradiating a light to a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group, if an azo polymerization initiator was used as a photopolymerization initiator, an inorganic phosphorus compound was used as a chain transferrer, and the polymerization was carried out by irradiating a light at a specific low light irradiation condition of $0.5\text{--}7\text{ W/m}^2$ in the presence of both of them, a water-soluble polymer with little insoluble portion and a high molecular weight could be obtained and the water-soluble polymer obtained could be appropriately utilized as aggregator, etc. Furthermore, the inventors discovered that even if the content ratio of the water-soluble monomer having a methacryloyl group in the monomer mixture was 35 mol% or less in this polymerization method, a water-soluble polymer with a high molecular weight and little insoluble portion could be obtained.

[0009] Also, the inventors discovered that in a continuous polymerization by this polymerization method using an actual apparatus, a water-soluble polymer with a high molecular weight and little insoluble portion could be smoothly manufactured by a simple operation, even without changing the light irradiation intensity (the kind of light source) each time patterns were switched. Also, the inventors discovered that the use of an azo polymerization initiator with a 10-hour half-life temperature of 50°C or higher in this polymerization method was more preferable for the manufacture of a water-soluble polymer with a high molecular weight and little insoluble portion. Also, it was discovered that if a second-step light irradiation was further applied under specific conditions after the above-mentioned light irradiation, the amount of unreacted monomers could be extremely reduced. Based on these knowledge, the present invention was completed.

[0010] In other words, the present invention is

(1) a method for manufacturing a water-soluble polymer characterized by the fact that in a method for manufacturing a water-soluble polymer by irradiating a light to an aqueous solution of a monomer mixture containing a water-soluble monomer having an acryloyl group and a water-soluble monomer having a methacryloyl group, the aqueous solution of the above-mentioned monomer mixture is polymerized in the presence of an azo polymerization initiator and an inorganic phosphorus compound by irradiating a light under the condition of a light irradiation intensity of $0.5\text{--}7\text{ W/m}^2$.

[0011] Then, the present invention is

- (2) the method for manufacturing a water-soluble polymer of the above-mentioned (1) characterized by the fact that the content ratio of the water-soluble monomer having a methacryloyl group in the monomer mixture is 5-35 mol%;
- (3) the method for manufacturing a water-soluble polymer of the above-mentioned (1) or (2) characterized by the fact that the monomer mixture is a monomer mixture containing a ternary salt and/or a quaternary salt of acrylamide and dialkylaminoalkyl methacrylate is included at a mole ratio of the former: the latter = 90:10-65:35;
- (4) the method for manufacturing a water-soluble polymer of any of the above-mentioned (1)-(3) characterized by the fact that the 10-hour half-life temperature of 50°C or higher is used as an azo polymerization initiator; and
- (5) the method for manufacturing a water-soluble polymer of any of the above-mentioned (1)-(4) characterized by the fact that after the light irradiation under the condition of the above-mentioned light irradiation intensity of 0.5-7 W/m², the light irradiation is further applied under the conditions of a light irradiation intensity higher than that and an integrated quantity of light of 70,000 J/m² or more.

[0012]

Embodiments of the invention

Next, the present invention is explained in detail. Also, acrylamide and methacrylamide are generally called (meth)acrylamide, acrylate and methacrylate are generally called (meth)acrylate, and acrylic acid and methacrylic acid are generally called (meth)acrylic acid. As the water-soluble monomer having an acryloyl group (hereinafter, called "water-soluble acryl group monomer") and the water-soluble monomer having a methacryloyl group (hereinafter, called "water-soluble methacryl group monomer") being used in the present invention, any monomers that have an acryloyl group or a methacryloyl group, are soluble in water, and are polymerized by irradiating a light in the presence of a photopolymerization initiator may be adopted. As the water-soluble acryl group monomer and the water-soluble methacryl group monomer usable in the present invention, for example, (meth)acrylamide such as (meth)acrylamide and methylol (meth)acrylamide; ternary salt such as dialkylaminoalkyl (meth)acrylate such as dimethylaminoethyl (meth)acrylate and these hydrochlorides, sulfates and quaternary salt such as alkyl halide adduct of these methyl chlorides and aryl halide adduct of benzyl chlorides; alkali metal salt or ammonium salt such as (meth)acrylic acid and these sodium salts; alkylamide alkane sulfonic acid such as acrylamide-2-methylpropane sulfonic acid and its alkali metal salt or ammonium salt; N substituted derivative of (meth)acrylamide such as N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N-ethyl(meth)acrylamide, N, N-

diethyl(meth)acrylamide; ternary salt such as hydrochloride and sulfate of N,N-dialkylaminoalkyl(meth)acrylamide and quaternary salt such as alkyl halide adduct of these methyl chlorides and aryl halide adduct such as benzoyl chlorides; hydroxyalkyl (meth)acrylate such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate, etc., are mentioned. In the present invention, one or more kinds of said (meth)acryl group monomers can be used.

[0013] Among the above-mentioned water-soluble (meth)acryl group monomers, in the present invention, the acrylamide as the water-soluble acryl group monomer and the ternary salt and/or the quaternary salt of dialkylaminoalkyl methacrylate as the water-soluble methacryl group monomer are preferable since a water-soluble polymer with excellent aggregation performance can be obtained. Of the ternary salt and the quaternary salt of dialkylaminoalkyl methacrylate being preferably used as the water-soluble methacryl group monomer, at least one kind of quaternary salt and ternary salt of N,N-dimethylaminoethyl methacrylate is especially preferably used since a water-soluble polymer with excellent aggregation performance is generated. The above-mentioned quaternary salt and ternary salt are preferably a shape of a quaternary salt being obtained by reacting with methyl chloride, etc., and a ternary salt such as hydrochloride, sulfate, and acetate.

[0014] The content ratio of the water-soluble acryl group monomer and the water-soluble methacryl group monomer in the monomer mixture is not particularly limited. The present invention can also be preferably applied to the case where the mole ratio of the water-soluble acryl group monomer:the water-soluble methacryl group monomer is 95:5-65:35, compared with the conventional method in which the copolymerization of both monomers is not favorably advanced by the conventional light irradiation, the insoluble portion content in the water-soluble polymer is large, and the water-soluble polymer with a high molecular weight cannot be obtained at this mole ratio.

[0015] In the present invention, in the range where the water solubility of the water-soluble polymer being obtained is not damaged (usually, the amount of 10 mol% or less to the total mole number of the entire monomer in the monomer mixture), along with the water-soluble acryl group monomer and the water-soluble methacryl group monomer, one or more kinds of (meth)acrylic acid ester such as (meth)acrylonitrile and methyl, ethyl, and propyl ester of (meth)acrylic acid, water-insoluble vinyl group monomer such as styrene, and other water-soluble vinyl group monomer (for example, dialkyldiallyl ammonium salt such as dimethyldiallyl ammonium chloride) may also be used in combination.

[0016] The concentration of the monomers in the aqueous solution of the monomer mixture containing the water-soluble acryl group monomer and the water-soluble methyl group monomer is preferably 20-90 mass%, more preferably 25-80 mass% in terms of smooth advance of the photopolymerization, handling characteristic of the water-soluble polymer being obtained, etc.

[0017] In the present invention, as the azo polymerization initiator, any azo polymerization initiator that can photopolymerize the above-mentioned monomer mixture under the condition of a light irradiation intensity of 0.5-7 W/m² can be used. As detailed examples of the azo polymerization initiator,

4,4'-azobis[4-cyanovaleric acid) (10-hour half-life temperature: 69°C, hereinafter, the temperature in the parenthesis shows a similar meaning);

2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine] (57°C);

dimethyl 2,2'-azobisisobutyrate (66°C);

2,2'-azobisisobutyronitrile (65°);

2,2'-azobis(2,4-dimethylvaleronitrile) (51°C);

2,2'-azobis(2-methylbutyronitrile) (67°C);

1,1'-azobis(cyclohexane-1-carbonitrile) (88°C);

2,2'-azobis{2-methyl-N-[2-(1-hydroxybutyl)]propionamide} (80°C);

2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (86°C);

2,2'-azobis(2-amidinopropane) hydrochloride (56°C);

2,2'-azobis[2-(5-methyl-2-imidazoline-2-yl)propane] hydrochloride (41°C);

2,2'-azobis[2-(2-imidazoline-2-yl)propane] hydrochloride (44°C);

2,2'-azobis[2-(2-imidazoline-2-yl)propane] sulfate (47°C);

2,2'-azobis[2-(2,4,5,6-tetrahydropyrimidine-2-yl)propane] hydrochloride (58°C);

2,2'-azobis{2-[1-(2-hydroxyethyl)-2-imidazoline-2-yl]propane} hydrochloride (60°C);

2,2'-azobis[2-(2-imidazoline-2-yl)propane] (61°C);

2,2'-azobis(2-methylbutane amidoximes) dihydrochloride (57°C);

1,1'-azobis(1-acetoxy-1-phenyl)ethane (61°C), etc., can be mentioned.

[0018] Among the above-mentioned azo polymerization initiators, an azo compound with a 10-hour half-life temperature of 50°C or higher is preferably used as an azo polymerization initiator since the solubility in water is high, a water-soluble polymer with no insoluble portion content or a small content, a water-soluble polymer with a high molecular weight is generated, the unreacted monomer in the water-soluble polymer is little, etc. An azo compound with a 10-hour half-life temperature of 50-90°C is more preferably used, and an azo compound with a 10-hour half-life temperature of 50-70°C is especially preferably used. In the present invention, as the

azo polymerization initiator, the above-mentioned azo compound may be used alone or in combination of two kinds or more. Among them, in the present invention, as the azo polymerization initiator, one or more kinds of 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(2-amidinopropane) hydrochloride, 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine], and 4,4'-azobis[4-cyanovaleric acid) are preferably used since a water-soluble polymer with more reduced unreacted monomer content is obtained, the molecular weight of the water-soluble polymer is high, and the solubility of the water-soluble polymer in water is good.

[0019] The amount of azo polymerization initiator is preferably 100-100,000 ppm, more preferably 200-5,000 ppm, and most preferably 500-3,000 ppm based on the mass of the aqueous solution of the monomer mixture.

[0020] Unless it is to the disadvantage of the present invention's purpose, along with the azo polymerization initiator, if necessary, one or more kinds of other photopolymerization initiators, for example, benzophenone group, benzoin group, benzoinalkyl ether group, acetophenone group, acylphosphine oxide group, etc., photosensitizers, for example, amine group photosensitizer such as triethanolamine and methyldiethanolamine may also be used in combination. If a ketone having a ring-shaped alkanol such as 1-benzoyl-1-hydroxycyclohexane is used along with the azo polymerization initiator, a water-soluble polymer in which the unreacted monomer content is reduced, the degree of polymerization is high, and the water solubility is high can be more smoothly obtained. In this case, the amount of ketone having a ring-shaped alkanol being used is preferably 0.5-30 mass% to the mass of the azo polymerization initiator.

[0021] Furthermore, in the present invention, an inorganic phosphorus compound is used along with the azo polymerization initiator. With the use of the inorganic phosphorus compound along with the azo polymerization initiator, the insoluble portion and the molecular weight are balanced, so that a water-soluble polymer with little insoluble portion and a high molecular weight can be obtained. As the inorganic phosphorus compound, any compound having a chain transfer action can be used, and as its detailed examples, hypophosphorous acid; phosphorous acid; hypophosphite such as sodium hypophosphite, potassium hypophosphite, and ammonium hypophosphite; phosphite such as sodium phosphite, potassium phosphite, and ammonium phosphite, etc., can be mentioned, and one or more kinds of those can be used. Among them, hypophosphite such as sodium hypophosphite, potassium hypophosphite, and ammonium

hypophosphite are preferably used since the insoluble portion in the water-soluble polymer being obtained is little.

[0022] The amount of inorganic phosphorus compound being used is preferably 5-500 ppm, more preferably 10-100 ppm, and most preferably 20-80 ppm.

[0023] Also, in the present invention, other components such as water-soluble organic solvents and surfactants may be used in the range where it is not to the disadvantage of the present invention's purpose, if necessary.

[0024] In the present invention, in a state in which the azo polymerization initiator and the inorganic phosphorus compound are included in the monomer mixture containing the water-soluble acryl group monomer and the water-soluble methacryl group monomer, the monomer mixture is polymerized by irradiating a light to said aqueous solution under a light irradiation intensity of $0.5-7 \text{ W/m}^2$. If the light irradiation intensity is less than 0.5 W/m^2 , the polymerization of the monomer mixture is not sufficiently carried out, or the degree of polymerization is scattered in the upper part and the lower part of the aqueous solution of the monomer mixture, so that a water-soluble polymer with uniform properties cannot be obtained and the unreacted monomer content in the water-soluble polymer being obtained is increased. On the other hand, if the light irradiation intensity exceeds 7 W/m^2 , a water-soluble polymer with high molecular weight cannot be obtained. The light irradiation intensity is preferably $0.75-7 \text{ W/m}^2$, more preferably $1-6 \text{ W/m}^2$.

[0025] As the light being irradiated, ultraviolet rays and/or visible lights are used, and among them, ultraviolet rays are preferably used. As the light source, any light source that can emit ultraviolet rays/visible lights that can photopolymerize the monomer mixture may be adopted, and for example, fluorescent chemical lamp, fluorescent blue lamp, metal halide lamp, high-pressure mercury lamp, etc., can be used.

[0026] The depth of the aqueous solution of the monomer mixture during the light irradiation is preferably 100 mm or less, more preferably 20-65 mm since a light arrives at the bottom of the aqueous solution the aqueous solution is entirely, smoothly polymerized. According to the method of the present invention, even if the depth of the aqueous solution of a vinyl group monomer is 50 mm or more, the vinyl group monomer is smoothly polymerized in the entire aqueous solution, so that an intended water-soluble polymer can be manufactured with good efficiency. Also, the polymerization reaction of the light irradiation may be a batch or

continuous type, and the continuous type is preferable since the productivity is excellent. The method of the present invention is suitable for the continuous type photopolymerization.

[0027] When the light irradiation starts, the temperature of the aqueous solution of the monomer mixture is set to a range of 0-20°C, especially 5-15°C since the concentration of the aqueous solution of the monomer mixture can be raised and an abrupt boiling of the aqueous solution of the monomer mixture can be prevented. The monomer mixture is polymerized by the light irradiation, and the temperature of the aqueous solution is slowly raised by the polymerization heat. The light irradiation time is preferably the time at which the polymerization rate of the monomer in the aqueous solution of the monomer mixture reaches 90% or more, more preferably 95% or more, and especially preferably 99% or more. The polymerization reaches 90% or more at a lapsed time of 10-200 min from the start of the light irradiation (the total lapsed time at which the aqueous monomer solution in the continuous polymerization passes through the light source is 10-200 min), though it may depend on the kind of water-soluble acryl monomer and water-soluble methacryl group monomer being included in the monomer mixture. Usually, if the temperature of the central part of the aqueous solution of the monomer mixture reaches a peak temperature, since the polymerization rate of the monomer mixture is 90% or more, a light may be irradiated at a light irradiation density of 0.5-7 W/m² until the temperature of said central part reaches the peak temperature or for longer time than that.

[0028] Through the above-mentioned light irradiation under the condition of a light irradiation intensity of 0.5-7 W/m², a water-soluble polymer with a high molecular weight and little insoluble portion is generated. Since the water-soluble polymer generated is generally a hydrous gel state, it may be used in each usage or may be used after cutting it finely into an appropriate size (preferably about 1-5 mm) and drying them or may be used in a powder shape by further pulverizing it after drying. The drying is preferably carried out at 60-130°C. The water-soluble polymer being obtained can be effectively used as an aggregator or other applications.

[0029] Also, in the present invention, the water-soluble polymer in the above-mentioned hydrous gel state generated by the light irradiation under the condition of a light irradiation intensity of 0.5-7 W/m² is recovered from the polymerization system, and if necessary, the light irradiation of the second step and its subsequent steps may be carried out under the conditions of a light irradiation intensity higher than the above-mentioned one and an integrated quantity of light of 70,000 J/m² or more. If the light irradiation of the second step and its subsequent steps is applied, since the unreacted monomer included in the water-soluble monomer generated by the light irradiation under the condition of a light irradiation intensity of 0.5-7 W/m² is further

polymerized, a water-soluble polymer with a very small content of the unreacted monomer can be obtained. Also, the light irradiation of the second step and its subsequent steps further raises the molecular weight of the water-soluble polymer and functions in the decomposition of the residual photopolymerization initiator in addition to the reduction of the amount of unreacted monomer.

[0030] In the light irradiation of the second step and its subsequent steps, the integrated quantity of light is preferably $90,000 \text{ J/m}^2$ or more, more preferably $100,000\text{--}2,000,000 \text{ J/m}^2$. If the integrated quantity of light of the second step and its subsequent steps exceeds $2,000,000 \text{ J/m}^2$, the solubility of the polymer being obtained in water is lowered. Also, the irradiation intensity in the light irradiation of the second step and its subsequent steps is preferably 1.5-3,000 times, more preferably 3-1,000 times of the initial light irradiation intensity. However, if the light irradiation intensity is too high, since a crosslinking of the water-soluble polymer generated, etc., is easily formed, the light intensity of the second step and its subsequent steps is preferably $10,000 \text{ W/m}^2$ or less. Since the integrated quantity of light (J/m^2) is attained as the product of the irradiation intensity (W/m^2) and the time (sec), the light irradiation time (sec) of the second step and its subsequent steps can be attained by dividing the integrated quantity of light (J/m^2) of the second step and its subsequent steps by the irradiation intensity (W/m^2) of the second step and its subsequent steps.

[0031] The light irradiation of the second step and its subsequent steps is preferably applied at a temperature higher than the 10-hour half-life temperature of the azo polymerization initiator used as a photopolymerization initiator, so that a water-soluble polymer in which the amount of unreacted monomer is further reduced can be obtained. The temperature during the light irradiation of the second step and its subsequent steps may be controlled by heating from the outside or may also be controlled by adjusting the initial temperature of the aqueous solution of the monomer mixture being provided to the polymerization in consideration of the temperature rise due to the polymerization heat, without heating from the outside. In general, the light irradiation of the second step and its subsequent steps is preferably carried out at a temperature of $60\text{--}100^\circ\text{C}$.

[0032] The light irradiation of the second step and its subsequent steps may be carried out using a reactor different from that of the initial light irradiation, however it is preferable to apply the light irradiation of the second step and its subsequent steps by using the same reactor after finishing the initial light irradiation in terms of temperature control of the light irradiation of the second step and its subsequent steps, simplicity of apparatuses, economical efficiency, etc.

[0033] The water-soluble polymer obtained by finishing the light irradiation of the second step and its subsequent steps exhibits a hydrous gel state similarly to the water-soluble polymer obtained by the initial light irradiation. The hydrous gel obtained may be used as it is in each usage or may be used after cutting it finely into an appropriate size (preferably about 1-5 mm) and drying them or may be used in a powder shape by further pulverizing it after drying. The hydrous gel is preferably dried at 60-130°C. The water-soluble polymer obtained has a high molecular weight and a good solubility in water, and the content of the unreacted monomer is considerably reduced.

[0034] In case the manufacturing method of the present invention is industrially applied, the continuous polymerization method is preferably adopted. According to the method of the present invention, in case the continuous polymerization is industrially carried out using an actual apparatus, since the light irradiation intensity (the kind of light source) is not required to be changed for each pattern switching, a water-soluble polymer with a high molecular weight of little insoluble portion can be manufactured by a simple operation. As the continuous polymerization method, various methods can be adopted, and among them, a method using an apparatus consisting of a continuous belt having a liquid reservoir part installed in an airtight chamber and a light source fixed to the upper part of the airtight chamber is preferably adopted. Specifically, the water solution of the monomer mixture is continuously supplied from one side of the continuous belt to maintain the intended depth. In this case, it is preferable to continuously supply an inert gas such as nitrogen into the airtight chamber to prevent the polymerization hindrance of the monomer due to oxygen. Said belt is continuously moved with the aqueous solution of the monomer mixture, and the aqueous solution of the monomer mixture is supplied under a fixed light source. The aqueous solution of the monomer mixture is ~~polymerized with the light being irradiated from said light source. In the initial light irradiation~~ and the light irradiation of the second step and its subsequent steps, as the light sources, a section that meets the initial light irradiation intensity and a section that meets the light irradiation of the second step and its subsequent steps and the integrated quantity of light may be installed. The polymer sheet being obtained is cut, pulverized, and dried following the ordinary method, to attain a powder product.

[0035] The water-soluble polymer being obtained by the method of the present invention can be effectively used in high-molecular flocculant for aggregating various kinds of waste waters, tackifier, sizing agent for paper-making, paper strength reinforcing agent, filtration accelerator,

fiber enhancer, dyeing aid, and other various applications and is especially suitable as a high-molecular flocculant.

[0036]

(Application examples)

Next, the present invention is explained in detail by application examples, however the present invention is not limited at all to the following application example. In the following example, 0.5% salt viscosity (mPa · s), insoluble portion (mL), and unreacted monomer content of the water-soluble polymers obtained in each example were attained by the following methods.

[0037] (0.5% salt viscosity of water-soluble polymer) Aqueous polymer solutions with a concentration of 0.5 mass% were prepared by dissolving the water-soluble polymers obtained in the following application examples or comparative examples into 4 mass% aqueous sodium chloride solution and stirred under the conditions of 25°C and 60 rpm by a B type viscometer, and the viscosity after 5 min from the stirring start was measured.

[0038] (Insoluble portion of water-soluble polymer) 400 mL aqueous polymer solutions with a concentration of 0.1 mass% were prepared by dissolving the water-soluble polymers obtained in the following application examples or comparative examples in an ion exchange water, and the total amount of the aqueous solutions was filtered through a sieve with a diameter of 20 cm and a mesh of 83. Insoluble portions remaining on the sieve were gathered, and the volume (mL) was measured.

[0039] (Content of unreacted monomers of water-soluble polymer) 2.0 g water-soluble polymer obtained in the following application examples or comparative examples was put into 20 mL acetone/water mixed solvent of 80/20 (volume ratio), held at 25°C for 16 hours, and extracted. The supernatant fluid after extracting was sampled, the amount of unreacted monomers was measured by gas chromatography, and the content (mass%) of the unreacted monomers to the water-soluble polymer was attained.

[0040] Application Example 1

(1) Distilled water was added to a monomer mixture containing 15 mol% quaternary salt of methyl chloride of dimethylaminoethyl acrylate (hereinafter, called "DMC") and 85 mol% acrylamide so that the total mass might be 1,100 g and the monomer concentration might be 37 mass%. It was charged into a Teflon (registered trademark)-lined container (reactor) with an inner diameter of 146 mm, and its pH was adjusted to 4.0 with hydrochloric acid. Then, while

maintaining the temperature of the aqueous solution at 5°C, a nitrogen bubbling was carried out for 15 min, so that an aqueous solution of the monomer mixture was prepared. At that time, the solution depth was 70 mm.

(2) 700 ppm 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide] ("VA-086" made by Wako Pure Chemical Industries, Ltd., 10-hour half-life temperature = 86°C) as a photopolymerization initiator and 60 ppm sodium hypophosphite based on the mass to the pure monomer portion were added to the aqueous solution of the monomer mixture of the above-mentioned (1), and the nitrogen bubbling was carried out for 15 min.

(3) Then, ultraviolet rays were irradiated at a light irradiation intensity of 1.6 W/m² for 120 min from the top of the reactor by a 10-W chemical lamp ("FL10BL" made by Toshiba Corporation), so that a hydrous gel-state polymer was obtained.

(4) The hydrous polymer obtained in the above-mentioned (3) was finely cut into a size with a particle diameter of about 3 mm, dried at 80°C for 5 hour by a hot-air dryer, and pulverized by a pulverizer, so that a powder-shaped polymer was obtained.

(5) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (4) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0041] Application Example 2

(1) Distilled water was added to a monomer mixture containing 15 mol% DMC and 85 mol% acrylamide so that the total mass might be 1,100 g and the monomer concentration might be 33 mass%. It was charged into the same reactor as that used in Application Example 1, and its pH was adjusted to 4.0 with hydrochloric acid. Then, while maintaining the temperature of the aqueous solution at 5°C, a nitrogen bubbling was carried out for 15 min, so that an aqueous solution of the monomer mixture was prepared. At that time, the solution depth was 70 mm.

(2) 700 ppm 2,2'-azobis(2-amidinopropane) dihydrochloride ("V-50" made by Wako Pure Chemical Industries, Ltd., 10-hour half-life temperature = 56°C) as a photopolymerization initiator and 35 ppm ammonium hypophosphite based on the mass to the pure monomer portion were added to the aqueous solution of the monomer mixture of the above-mentioned (1), and the nitrogen bubbling was carried out for 15 min.

(3) Then, ultraviolet rays were irradiated at a light irradiation intensity of 1.6 W/m^2 for 120 min from the top of the reactor similarly to Application Example 1, so that a hydrous gel-state polymer was obtained.

(4) The hydrous polymer obtained in the above-mentioned (3) was finely cut, dried, and pulverized similarly to Application Example 1, so that a powder-shaped polymer was obtained.

(5) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (4) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0042] Application Example 3

(1) A powder-shaped polymer was obtained by operations similar to (1)-(4) of Application Example 1 except for changing the sodium hypophosphite to 35 ppm in (2) of Application Example 1 and setting the light irradiation intensity to 4.2 W/m^2 in (3).

(2) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (1) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0043] Comparative Example 1

(1) A powder-shaped polymer was obtained by the same operations as (1)-(4) of Application Example 1 except for adding 700 ppm 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide] ("VA-086" made by Wako Pure Chemical Industries, Ltd.) and not adding the sodium hypophosphite in (2) of Application Example 1.

(2) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (1) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0044] Comparative Example 2

(1) A powder-shaped polymer was obtained by the same operations as (1)-(4) of Application Example 2 except for adding 700 ppm 2,2'-azobis(2-amidinopropane) dihydrochloride ("V-50" made by Wako Pure Chemical Industries, Ltd.) and not adding the ammonium hypophosphite in (2) of Application Example 2.

(2) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (1) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0045] Comparative Example 3

(1) A powder-shaped polymer was obtained by the same operations as (1)-(4) of Application Example 1 except for adding 700 ppm 2,2'-azobis[2-(2-imidazoline-2-yl)propane] hydrochloride ("VA-044" made by Wako Pure Chemical Industries, Ltd., 10-hour half-life temperature = 44°C) instead of the 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide] ("VA-086" made by Wako Pure Chemical Industries, Ltd.) and not adding the sodium hypophosphite in (2) of Application Example 1.

(2) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (1) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0046] Comparative Example 4

(1) Distilled water was added to a monomer mixture containing 15 mol% DMC and 85 mol% acrylamide so that the total mass was 1,100 g and the monomer concentration was 30 mass%. It was charged into the same reactor as that used in Application Example 1, and its pH was adjusted to 4.0 with hydrochloric acid. Then, while maintaining the temperature of the aqueous solution at 5°C, a nitrogen bubbling was carried out for 15 min, so that an aqueous solution of the monomer mixture was prepared. At that time, the solution depth was 70 mm.

(2) 50 ppm 1-hydroxycyclohexyl-phenylketone ("Irgacure 184" made by Chiba Specialty K.K.) based on the mass to the pure monomer portion was added as a photopolymerization initiator to the aqueous solution of the monomer mixture of the above-mentioned (1), and the nitrogen bubbling was carried out for 15 min.

(3) Then, ultraviolet rays were irradiated at a light irradiation intensity of 5 W/m² for 120 min from the top of the reactor similarly to Application Example 1, so that a hydrous gel-state polymer was manufactured. Said hydrous polymer was finely cut, dried, and pulverized similarly to Application Example 1, so that a powder-shaped polymer was obtained.

(4) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (3) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0047] Comparative Example 5

(1) A powder-shaped polymer was obtained by operations similar to (1)-(4) of Application Example 1 except for adding 35 ppm trimethanolamine (chain transferrer) instead of the sodium hypophosphite in (2) of Application Example 1.

(2) When the 0.5-% salt viscosity and the insoluble portion of the powder-shaped polymer obtained in the above-mentioned (1) were measured by the above-mentioned methods, the results shown in the following Table I were obtained.

[0048]

(Table I)

	Photopolymerization initiator		Chain transferrer		Light irradiation intensity (W/m ²)	Water-soluble polymer	
	Kind ¹⁾	Amount used (ppm)	Kind ²⁾	Amount used (ppm)		0.5% salt viscosity (mPa·s)	Insoluble portion (mL)
Application Example 1	A	700	a	60	1.6	70	0
Application Example 2	B	700	b	35	1.6	50	0
Application Example 3	A	700	a	35	4.2	58	0
Comparative Example 1	A	700	-	-	1.6	30	250
Comparative Example 2	B	700	-	-	1.6	68	90
Comparative Example 3	C	700	-	-	1.6	55	20
Comparative Example 4	D	50	-	-	1.6	54	100
Comparative Example 5	A	700	c	35	1.6	40	200

1) Kind of photopolymerization initiator:

A: 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide]

B: 2,2'-azobis(2-amidinopropane) dihydrochloride

C: 2,2'-azobis[2-(2-imidazoline-2-yl)propane] hydrochloride

D: 1-hydroxycyclohexyl-phenylketone

2) Kind of chain transferrer:

a: Sodium hypophosphite

b: Ammonium hypophosphite

[0049] As seen from the results of the above-mentioned Table I, in Application Examples 1-3, the aqueous solution of the monomer mixture containing a water-soluble acryl group monomer

(acrylamide) and a water-soluble methacryl group monomer (DMC) is polymerized by irradiating a light at a light irradiation intensity to $0.5-7 \text{ W/m}^2$ in the presence of an azo polymerization initiator and an inorganic phosphorous compound, so that water-soluble polymers in which the 0.5-% salt viscosity is high, the molecular weight is high, and no insoluble portion is included can be obtained. On the contrary, in Comparative Examples 1-3, the photopolymerization was carried out using only the azo polymerization initiator without using an inorganic phosphorus compound, the water-soluble polymers generated included a large amount of insoluble portions. Furthermore, the water-soluble polymer obtained in Comparative Example 1 had a low 0.5% salt viscosity, and the molecular weight is low compared with the water-soluble polymers obtained in Application Examples 1 and 2.

[0050] Also, in Comparative Example 4, using 1-hydroxycyclohexyl-phenylketone as the photopolymerization initiator, the photopolymerization is carried out in the absence of an inorganic phosphorus compound, a large amount of insoluble portions is included in the water-soluble polymer. Furthermore, in Comparative Example 5, although the same azo polymerization initiator as that of Application Example 1, since triethanolamine is used as the chain transferrer instead of the inorganic phosphorus compound, the water-soluble polymer generated includes a large amount of insoluble portion, the 0.5-% salt viscosity is low, and the molecular weight is small.

[0051] Application Example 4

(1) After manufacturing a hydrous gel-state polymer by the same operations as (1)-(3) of Application Example 1, said hydrous gel-state polymer was put into a reactor and irradiated for 30 min by ultraviolet rays at a light irradiation intensity of 120 W/m^2 (an integral quantity of light = $216,000 \text{ J/m}^2$) by using a 400-W black light ("H400BL-L" made by Toshiba Corporation), so that a hydrous gel-state polymer was obtained.

(2) The hydrous polymer obtained in the above-mentioned (1) was finely cut, dried, and pulverized similarly to (4) of Application Example 1, so that a powder-shaped polymer was obtained. When the content of unreacted monomers in the powder-shaped water-soluble polymer obtained in this manner was measured by the above-mentioned method, a very infinitesimal amount of 0.16 mass% was obtained.

[0052] Application Example 5

(1) After manufacturing a hydrous gel-state polymer by the same operations as (1)-(3) of Application Example 2, said hydrous gel-state polymer was put into a reactor and irradiated for

30 min by ultraviolet rays at a light irradiation intensity of 120 W/m^2 (an integral quantity of light = $216,000 \text{ J/m}^2$), so that a hydrous gel-state polymer was obtained.

(2) The hydrous polymer obtained in the above-mentioned (1) was finely cut, dried, and pulverized similarly to (4) of Application Example 1, so that a powder-shaped polymer was obtained. When the content of unreacted monomers in the powder-shaped water-soluble polymer obtained in this manner was measured by the above-mentioned method, a very infinitesimal amount of 0.16 mass% was obtained.

[0053]

Effects of the invention

According to the present invention, a water-soluble polymer with little insoluble portion, excellent water solubility, and a high molecular weight can be manufactured with good productivity by a simple operation. In the polymerization method of the present invention, in case a continuous polymerization is carried out using an actual apparatus, a water-soluble polymer with a high molecular weight and little insoluble portion can be/10 manufactured with good efficiency by a simple operation, even without changing the light irradiation intensity (the kind of light source) each time patterns are switched. Furthermore, in the present invention, in case the light irradiation of the second step and its subsequent steps is further carried out, the amount of unreacted monomers in the water-soluble polymer can be reduced to a very small amount.